U.S. DEPARTMENT OF THE INTERIOR U.S. GEOLOGICAL SURVEY

Thermal maturity patterns (CAI and %R_o) in the Ordovician and Devonian rocks of the Appalachian basin in New York State

David J. Weary¹ Robert T. Ryder¹ and Richard Nyahay²

Open-File Report 00-496

This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards and stratigraphic nomenclature. Any use of trade names is for descriptive purposes only and does not imply endorsement by the USGS.

- 1 U.S. Geological Survey, Reston, Virginia 20192
- 2 New York State Geological Survey, Albany, New York 12230

CONTENTS

F	Page
Introduction	1
	2 5
Stratigraphy of sampled intervals	5
Thermal maturity results	8
Ordovician data set	8
Devonian data set	10
Conclusions	15
References cited	16
ILLUSTRATIONS	
Figure 1. Location of wells and surface localities sampled in this study Figure 2. Stratigraphic relationships of the Black River and Trenton	3
Groups in New York with ranges of conodont sample collections recovered in this study	6
rocks in New York with conodont sample collections recovered in this study	7
Figure 4. Middle and Upper Ordovician Conodont Alteration Index (CAI)	,
Isograds based largely on new data collected in this study Figure 5. Comparison of locations of Middle/Upper Ordovician and Lower	9
Silurian gas fields in New York with Ordovician Conodont Alteration Index (CAI) isograds from this study	11
on new data collected in this study	12
Figure 7. Comparison of locations of Upper Silurian/Devonian oil and gas fields in New York with Devonian Conodont Alteration Index (CAI)	
isograds from this study	13
Figure 8. Devonian vitrinite reflectance value (%R _o) based on new data collected in this study	14
TABLES	
Table 1. Data for conodonts recovered from Ordovician samples from the subsurface of New York(separate file)	20
Table 2. Data for conodonts recovered from Devonian samples from the subsurface of New York(separate file)	28
Table 3. Thermal maturity (CAI) data from Ordovician samples from the	
subsurface of New York(separate file)	. 35
samples from the subsurface of New York(separate file)	. 37

INTRODUCTION

The classic study by Epstein and others (1977), using conodont alteration index (CAI) isograds, is the established standard for evaluating thermal maturity patterns of lower and middle Paleozoic rocks and associated oil and gas accumulation in the Appalachian basin. Maps from the Epstein and others (1977) and Harris and others (1978) studies show basin wide thermal maturity patterns for the Ordovician, Silurian through Middle Devonian, and Upper Devonian through Mississippian. Despite the value of these maps, they have a strong bias toward outcrop samples and, in many parts of the basin, CAI isograds have been extrapolated several hundreds of miles without being constrained by subsurface control points. Wandrey and others (1997) converted the CAI isograds of Harris and others (1978) to vitrinite reflectance equivalents (VTE) for the Ordovician of the central Appalachian basin; however, few new data points were added. Also, several vitrinite reflectance (%R₀) maps are available for evaluating thermal maturity patterns in the Appalachian basin but they are limited to smaller areas than the CAI-based maps. Among the best examples of these vitrinite reflectance maps are those of Upper Devonian black shale units by Streib (1981) and Boswell (1996) and of Pennsylvanian coal beds by Chyi and others (1987) and Zhang and Davis (1993).

The objective of this study is to enhance existing thermal maturity maps in New York State by establishing: 1) new subsurface CAI data points for the Ordovician and Devonian and 2) new R_0 and Rock Eval subsurface data points for Middle and Upper Devonian black shale units. The thermal maturity of the Ordovician and Devonian rocks is of major interest because they contain the source for most of the unconventional natural gas resources in the basin. Thermal maturity patterns of the Middle Ordovician

Trenton Group are evaluated here because they closely approximate those of the overlying Ordovician Utica Shale that is believed to be the source rock for the regional oil and gas accumulation in Lower Silurian sandstones (Jenden and others, 1993; Ryder and others, 1998). Improved CAI-based thermal maturity maps of the Ordovician are important to identify areas of optimum gas generation from the Utica Shale and to provide constraints for interpreting the origin of oil and gas in the Lower Silurian regional accumulation, in particular, its basin-centered part (Ryder, 1998). Thermal maturity maps of the Devonian will better constrain burial history-petroleum generation models of the Utica Shale, as well as place limitations on the origin of regional oil and gas accumulation in Upper Devonian sandstone and Middle to Upper Devonian black shale.

New York State is the first area in the Appalachian basin where collecting, processing, and analysis of subsurface drill-hole cuttings and core samples have been completed on a large-scale to recover conodont elements and assign CAI values to them. This investigation was a cooperative effort between the U.S. Geological Survey (USGS) and the New York State Geological Survey. Additional cooperative investigations in Pennsylvania (USGS–Pennsylvania Topographic and Geologic Survey), West Virginia (USGS–West Virginia Geological Survey) and Ohio (USGS–Ohio Division of Geological Survey), are at various stages of completion.

METHODOLOGY

Drill-hole cuttings (n=106) and selected cores (n=3) were collected by one of us (R.N.) at the New York State Geological Survey's sample storage facility in Albany.

Sixty drill holes in 24 counties were sampled. Locations of the wells sampled are shown on figure 1. Where possible, Ordovician and Devonian intervals were collected from the

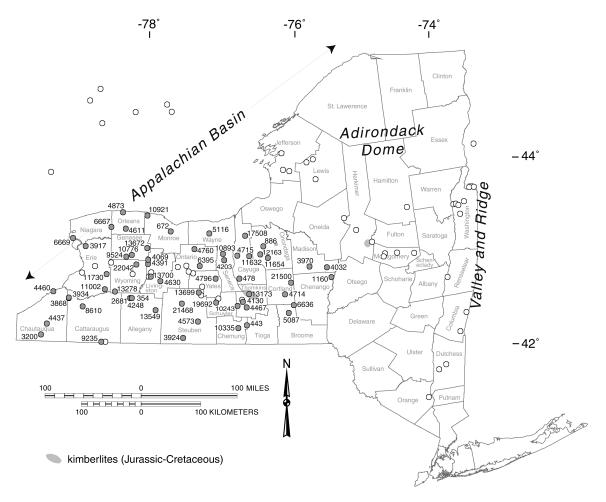


Figure 1. Map of New York showing location of wells () and surface localities sampled () in this study. Wells labeled with American Petroleum Institute (API) suffix numbers. Surface sample data from Harris and others (1978). Location of kimberlites shown because they are discussed later.

same drill hole (well). The total collection (n=109) consists of: 1) carbonate (limestone) samples from the Middle Ordovician Trenton Group (n=43), 2) carbonate (chiefly limestone and calcareous shale) samples from selected Devonian units (n=44), and 3) black shale samples primarily from the Middle Devonian Marcellus Shale (n=22). Each sample weighed about 100 g and consisted of rock fragments >20 mesh. Most samples were composites from 50 to 200 ft of stratigraphic section. The carbonate samples were sent to the USGS in Reston, Virginia, where they were processed and analyzed for conodonts. Devonian black shale samples were sent to Humble Geochemical Services¹, Humble, Texas where they were processed and analyzed for total organic carbon (TOC), Rock Eval parameters, and vitrinite reflectance.

Conodonts recovered were visually compared with a set of conodont color standards provided by A.G. Harris of the U.S. Geological Survey and assigned a CAI value. Samples exhibiting a range of CAI values were assigned a minimum and maximum value. Since variations in CAI within a sample can be caused by very local hydrothermal alteration, the CAI minimum value was assumed to most accurately reflect regional thermal effects, as per Epstein and others (1977) and Rejebian and others (1987), and was the value used for the succeeding maps (figs. 4-7). The conodont samples are reposited in the collections of the U.S. Geological Survey and filed under Cambrian-Ordovician (CO) or Silurian-Devonian (SD) collection numbers (see tables 1 and 2).

The maps, figs. 1 and 4-8, were constructed by plotting points in ARC/INFO over a digital base map, using latitude/longitude coordinates from the New York State

¹ Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

4

.

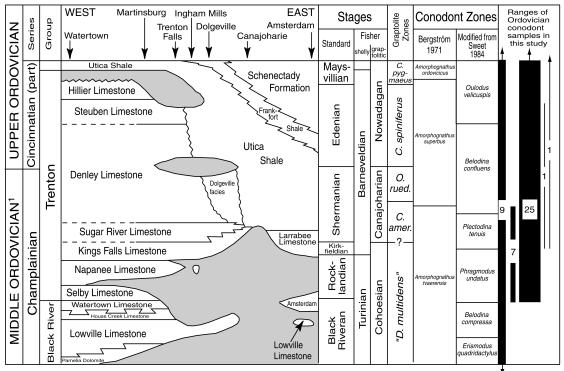
Geological Survey well database. The points were then attributed with American Petroleum Institute (API) numbers and minimum and maximum CAI values. Data points and CAI isograd contours from Harris and others (1978) were captured by scanning and georegistering the maps, then tracing and attributing the points and lines in ARC/INFO. The coverages were then projected to State Plane Projection and exported to ARCVIEW version 3.1 for ease of manipulation and graphic display.

RESULTS

STRATIGRAPHY OF SAMPLED INTERVALS

All Ordovician samples used in this study were identified on well logs by the New York Geological Survey as Trenton Group, with no subdivision. No attempt was made to identify any of the samples to formational level. All 43 carbonate samples from the Trenton Group yielded conodonts, in absolute abundances ranging from 1 element fragment up to 136 elements. Ranges of conodont species recovered indicate that all of the samples are consistent with the age of the Trenton Group, with 36 samples not necessarily restricted to the Trenton, and 7 samples restricted to that range (fig. 2). Table 1 contains detailed species composition, abundance, biostratigraphic position, and other data from the conodont collections recovered.

Devonian samples were selected from various carbonate units, predominantly in the Upper Devonian. Where Upper Devonian samples were not available or were ambiguous, samples were taken in Middle or Lower Devonian carbonates. Twenty-five of the 44 carbonate samples from the Devonian yielded conodonts, in absolute abundances ranging from 1 element fragment up to 262 elements. Recovered conodont species indicate ages ranging from Late Silurian/Early Devonian to late Devonian. A single sample



¹Due to the recent decision of the International Commission on Stratigraphy (Webby,1998), the entire Black River and Trenton Groups would now be considered Upper Ordovician. We follow the traditional Series assignments here to be consistent with longtime usage.

Figure 2. Stratigraphic relationships of the Black River and Trenton Groups in New York with ranges of conodont sample collections recovered in this study. Numbers in black bars indicate number of samples representing each range, total = 43. Stratigraphy from Bergström (1986, Fig. 2)

is possibly Late Silurian in age (Table 2,USGS sample number 12703-SD) but was retained in the Devonian sample set, as the CAI value from it is consistent with those from neighboring samples. Figure 3 illustrates the numbers, successful conodont yield, and approximate position within the regional stratigraphy of samples in the Devonian set. Table 2 contains detailed species composition, abundance, biostratigraphic position, and other data from the conodont collections recovered.

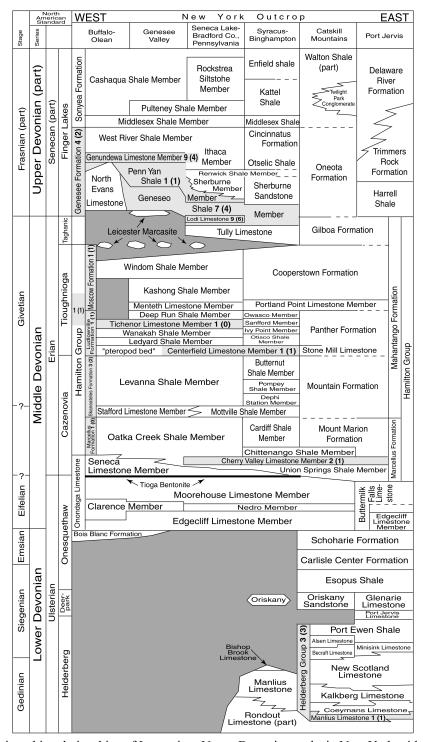


Figure 3. Stratigraphic relationships of Lower into Upper Devonian rocks in New York with conodont sample recoveries from this study. Stratigraphic units sampled in light gray. Hiatuses in dark gray. Number of condont samples processed from each unit in plain numerals, samples yielding condonts in parentheses. Total Devonian samples = 44. Stratigraphy from Oliver and others (1967, fig. 4)

THERMAL MATURITY RESULTS

Ordovician Data Set

The new CAI data for the Ordovician samples are plotted in figure 4 and contoured as isograds. For comparison, the CAI isograds from Harris and others (1978) are also shown. The earlier data were chiefly from surface collections along the Adirondack Dome to the north and east, the Valley and Ridge rocks in the eastern part of the state, and central Pennsylvania to the south (figure 1), giving little control over the Appalachian basin in central and western New York. CAI isograds in Harris and others (1978) range from 2 in the west to 5 in the east and trend smoothly in a southwest to northeast direction. Although isograds defined from this study approximate those of Harris and others (1978) in eastern and western New York, they differ in central New York, where they are shifted markedly further west by more than 100 km and are more tightly grouped, particularly in the CAI 3 to 4.5 range. This close grouping of isograds reflects a steeper thermal gradient than previously noted by Harris and others (1978). A similarly abrupt east-to-west increase in thermal maturity across New York was noted by Johnsson (1986) in the Middle Devonian Tioga metabentonite using clay-mineral diagenesis and apatite fission-track age data. Moreover, our data show an adjoining relatively low thermal maturity embayment that protrudes southeastward from Herkimer County.

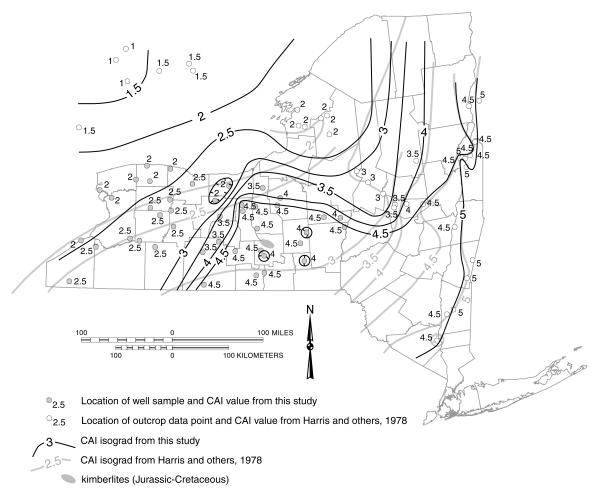


Figure 4. Middle and Upper Ordovician Conodont Alteration Index (CAI) isograds from data used in this study. The CAI isograds are based on data from this study and that of Harris and others (1978)

At first glance this shape in the isograds appears to mimic the isopach contours for Upper and Middle Ordovician clastic rocks, and Silurian carbonate and evaporite rocks in New York (Miller, 1975; de Witt and others, 1975). However, the CAI 3 to 4.5 isograds cut across the isopach at a high angle in west-central New York and CAI 4.5 to 5 isograds are centered over the thinnest isopachs. A better match between isograd and isopach

patterns is achieved with the Middle Ordovician through Permian isopachs (Harris and others, 1978) but even in this situation CAI 3 to 4.5 isograds cut sharply across the isopachs in west-central New York. These comparisons between isograd and isopach patterns in New York are complicated by Paleozoic and post-Paleozoic uplift of the Appalachians and the erosion of parts of the Upper Ordovician and Silurian as well as all pre-existing Carboniferous and Permian strata.

The CAI isograds for the Ordovician samples are plotted on figure 5, along with the locations of Middle and Upper Ordovician and Lower Silurian gas fields. The gas fields are located largely between the 2.5 and 4.5 CAI isograds (%Ro ~1.5 and 4) which is broadly consistent with the range of thermal maturity indices commonly cited for the "window" of dry natural gas generation and preservation (Dow, 1977; Harris and others, 1978; Tissot and Welte, 1984).

Devonian data set

The CAI data and interpreted isograds for the Devonian samples are plotted in figure 6 along with the CAI isograds from Harris and others (1978) for comparison. The distribution and shape of the isograds in this study change significantly from those of the Harris and others (1978) plot because of additional sample localities, especially in north-central and south-central New York. As noted for the Ordovician data, the CAI 2 to 3 isograds are shifted farther westward about 50 to 75 kilometers than shown in Harris and others (1978) and furthermore, there is a hint that they are more tightly grouped in the same approximate locations as the Ordovician isograds in the 3 to 4.5 range. Again the isograds reflect higher paleotemperatures and a steeper paleotemperature gradient in central New York than was recognizable given the data used by Harris and others (1978).

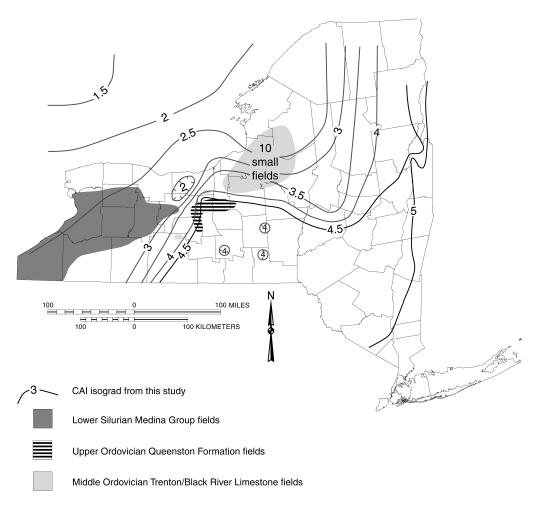


Figure 5. Comparison of locations of Middle/Upper Ordovician and Lower Silurian gas fields in New York with Ordovician Conodont Alteration Index (CAI) isograds from this study. Gas field data from New York State Department of Environmental Conservation (1986).

Although the shapes of the Devonian isograds and overburden isopachs (Devonian through Permian; Harris and others, 1978) are more similar than in the Ordovician example, the isograds still cut sharply across the isopachs in central New York.

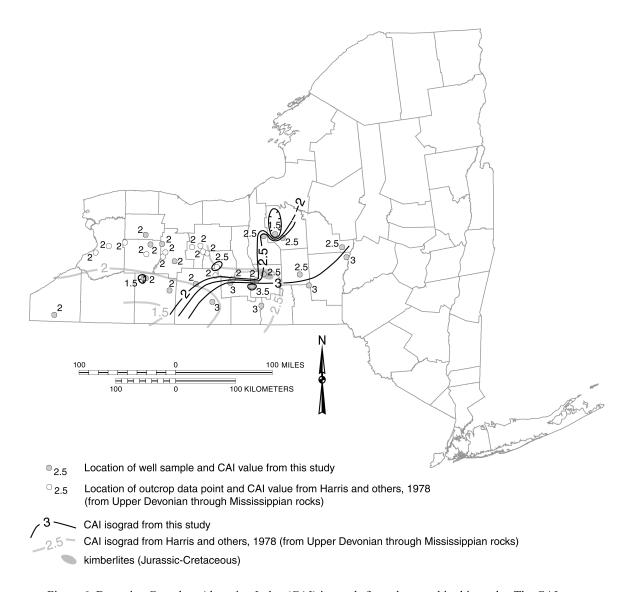


Figure 6. Devonian Conodont Alteration Index (CAI) isograds from data used in this study. The CAI isograds are based on data from this study and that of Harris and others (1978)

The CAI isograds for the Devonian samples are plotted on figure 7 along with locations of Upper Silurian and Devonian oil and gas fields. Oil fields are located in the western part of the area where CAI values are 2 or less (%Ro ~1 or less). The eastern limit of oil fields in the western part of Steuben County has a CAI value of 2.5 (%Ro

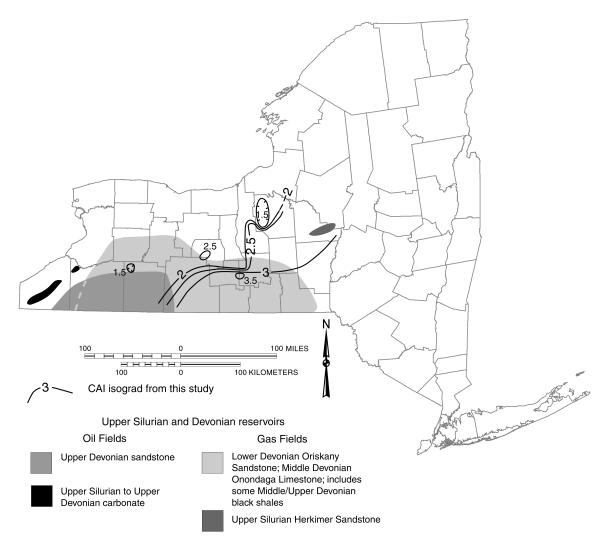


Figure 7. Comparison of locations of Upper Silurian/Devonian oil and gas fields in New York with Devonian Conodont Alteration Index (CAI) isograds from this study. Oil and gas field data from New York State Department of Environmental Conservation (1986).

~1.5). Gas fields are found mainly in south-central and west-central New York where CAI

values range from 2 to 3.5 (%Ro ~1 to 2.7). These CAI isograds are broadly consistent with the range of thermal maturity indices commonly cited for the "window" of oil and natural gas generation and preservation (Dow, 1977; Harris and others, 1978; Tissot and Welte, 1984).

Vitrinite reflectance values of black shale samples from the Devonian (mainly Middle Devonian Marcellus Shale) are shown on figure 8. Percent Ro values range from

0.45 in the west (Genesee County) to over 2.12 in the east (Broome County), with a gradual west to east increase. The %Ro contour patterns are roughly compatible with the CAI isograds including the grouping of the contours in central New York.

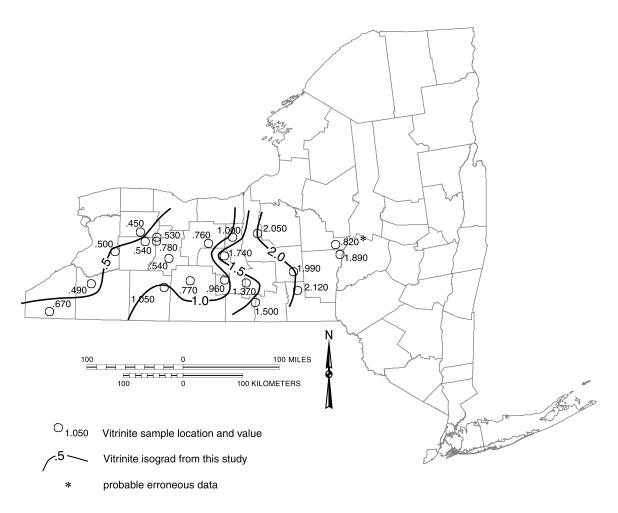


Figure 8. Devonian vitrinite reflectance value (%Ro) contours based on data collected in this study.

In

most localities where both %Ro and CAI measurements are available, the %Ro values indicate a slightly higher level of thermal maturity than the CAI values. Overall, the %Ro contours agree with the oil and gas field locations about as well as the CAI isograds.

CONCLUSIONS

Assuming a geothermal gradient in the 20° to 30° C/km range that is typical of foreland basin settings, Ordovician CAI isograds in New York (figure 4) imply much higher paleotemperatures than can be explained by the 10,000 to 12,000 ft (3 to 3.7 km) of existing overburden. Moreover, the gradual thickness changes in overburden cannot account for the steep thermal maturity gradient in central New York as indicated by the tight grouping of CAI isograds. Thus, burial by the Taconic clastic wedge could not have been a controlling factor in the distribution of observed CAI isograds. The same is true for the Devonian CAI isograds and %Ro contours (figures 6, 8) which indicate much higher paleotemperatures than expected from the 6000 to 8,000 ft (1.8 to 2.4 km) of existing overburden. Thermal maturity indices measured and interpreted by Friedman and Sanders (1982), Lakatos and Miller (1983), and Johnsson (1986) lead to similar conclusions.

Several explanations for the high thermal maturity are possible: 1) burial beneath thick Carboniferous and Permian overburden that has since been eroded, 2) igneous activity, and 3) regional fluid flow. Johnsson (1986) favors burial heating by 4 km of Carboniferous overburden as the cause of the higher-than-expected paleotemperatures. Although discounted by Johnsson (1986), we suggest that an elevated geothermal flux associated with emplacement of Cretaceous-age ultramafic intrusions in central and eastern New York (Kay and others, 1983) (figures 1,4,6) may be a contributing factor. The intrusions are small, but they could broaden with depth into pluton-sized bodies. Also, the expected high temperatures of emplacement (~900° to 1000° C at 80 to 90 km; Kay and others, 1983) may be sufficient to elevate the regional geothermal gradient. Regional fluid flow is probably not the cause of the high thermal maturity because

estimated rates of flow of basin-derived fluids appear to be too high to leave a thermal imprint on CAI values (Dorobek, 1989).

REFERENCES CITED

- Bergström, S.M., 1971, Conodont biostratigraphy of the Middle and Upper Ordovician of Europe and eastern North America, *in* Sweet, W.C. and Bergström, S.M., eds., Symposium on conodont biostratigraphy, Geological Society of America Memoir 127, p. 83-161.
- Bergström, S.M., 1986, Stratigraphic classification of the Trenton Group and associated strata in New York A North American Middle Ordovician standard succession, *in* Miller, M.A., ed., A field excursion to the Trenton Group (Middle and Upper Ordovician) and Hamilton Group (Middle Devonian) localities of New York, and a survey of their chitinozoans: in conjunction with the American Association of Stratigraphic Palynologists and Commission Internationale de Microflore de Paléozoïque, 3rd joint meeting, October 29 November 1, 1986, 118 pp.
- Boswell, R., 1996, Play Uds: Upper Devonian black shales, *in* Roen, J.B. and Walker, B.J., eds., The atlas of major Appalachian gas plays: West Virginia Geological and Economic Survey Publication V-25, p. 93-99.
- Chyi, L.L., Barnett, R. G., Burford, A.E., Quick, T.J., and Gray, R.J., 1987, Coalification patterns of the Pittsburgh coal: Their origin and bearing on hydrocarbon maturation: International Journal of Coal Geology, v. 7, no. 1, p. 69-83.

- de Witt, W., Jr., Perry, W.J., and Wallace, L.G., 1975, Oil and gas data from Devonian and Silurian rocks in the Appalachian Basin: U.S. Geological Survey, Folio of Appalachian Basin oil and gas data, Map I-917B, sheets 1-4.
- Dorobek, S., 1989, Migration of orogenic fluids through the Siluro-Devonian Helderberg Group during late Paleozoic deformation: constraints on fluid sources and implications for thermal histories of sedimentary basins: Tectonophysics, v. 159, p. 25-45.
- Dow, W.G., 1977, Kerogen studies and geological interpretations: Journal of Geochemical Exploration, v. 7, p. 79-99.
- Epstein, A.G., Epstein, J.B., and Harris, L.D., 1977, Conodont color alteration an index to organic metamorphism: U.S. Geological Survey Professional Paper 995. 27 pp.
- Friedman, G.M., and Sanders, J.E., 1982, Time-temperature-burial significance of Devonian anthracite implies former great (~6.5 km) depth of burial of Catskill Mountains, New York: Geology, v. 10, p. 93-95.
- Harris, A.G., Harris, L.D., and Epstein, J.B., 1978, Oil and gas data from Paleozoic rocks in the Appalachian basin: Maps for assessing by hydrocarbon potential and thermal maturity (conodont color alteration isograds and overburden isopachs): U.S. Geological Survey Miscellaneous Investigation Series Map I-917-E, 4 sheets with text.
- Jenden, P.D., Drazan, D.J., and Kaplan, I.R., 1993, Mixing of thermogenic natural gases in natural gas in northern Appalachian basin: American Association of Petroleum Geologists Bulletin, v. 77, p. 980-998.
- Johnsson, M.J., 1986, Distribution of maximum burial temperatures across northern Appalachian Basin and implications for Carboniferous sedimentation patterns: Geology, v. 14, p. 384-387.

- Kay, S.M., Snedden, W.T., Foster, B.P., and Kay, R.W., 1983, Upper mantle and crustal fragments in the Ithaca Kimberlites: Journal of Geology, v. 91, p. 277-290.
- Lakatos, S. and Miller, D.S., 1983, Fission track analysis of apatite and zircon defines burial depth of 4 to 7 km for lowermost Upper Devonian, Catskill Mountains, New York:

 Geology, v. 11, p. 103-104.
- Miller, R.L., 1975, Oil and gas data from the Upper and Middle Ordovician rocks in the Appalachian Basin: U.S. Geological Survey, Folio of Appalachian Basin oil and gas data, Map I-917C.
- New York State Department of Environmental Conservation, 1986, New York State oil and gas fields: New York State Department of Environmental Conservation, 1 sheet, scale 1:250,000.
- Oliver, W.A., Jr., de Witt, W., Jr., Dennison, J.M., Hoskins, D.M., and Huddle, J.W., 1967,

 Devonian of the Appalachian Basin, United States, *in* Oswald, D.H., ed., International

 Symposium on the Devonian System, Calgary: Alberta Society of Petroleum Geologists,

 pp. 1001-1040.
- Rejebian, V.A., Harris, A.G., and Huebner, J.S., 1987, Conodont color and textural alteration: an index to regional metamorphism, contact metamorphism, and hydrothermal alteration: Geological Society of America Bulletin, v. 99, p. 471-479.
- Ryder, R.T., 1998, Characteristics of discrete and basin-centered parts of the Lower Silurian regional oil and gas accumulation, Appalachian basin: Preliminary results from a data set of 25 oil and gas fields: U.S. Geological Survey Open-File Report 98-216, 71 p.

- Ryder, R.T., Burruss, R.C., and Hatch, J.R., 1998, Black shale source rocks and oil generation in the Cambrian and Ordovician of the central Appalachian basin, USA: American Association of Petroleum Geologists Bulletin, v. 82, p. 412-441.
- Streib, D.L., 1981, Distribution of gas, organic carbon, and vitrinite reflectance in the eastern Devonian gas shales and their relationship to the geologic framework: U.S. Department of Energy, Morgantown Energy Technology Center Report METC/08216-1276, 262 p.
- Sweet, W.C., Graphic correlation of upper Middle and Upper Ordovician rocks, North American Midcontinent Province, U.S.A.: *in* Bruton, D.L., ed., Aspects of the Ordovician System, Paleontological contributions from the University of Oslo, no. 295, p. 23-35.
- Tissot, B.P., and Welte, D.H., 1984, Petroleum formation and occurrence: New York, Springer-Verlag, 699 p.
- Wandrey, C.J., Ryder, R.T., Nuccio, V.F., and Aggen, K.L., 1997, The areal extent of continuous type gas accumulations in Lower Silurian Clinton sands and Medina Group sandstones of the Appalachian basin and the environments affected by their developments: U.S. Geological Survey Open-File Report 97-272, scale 1:500,000 2 sheets.
- Webby, B.D., 1998, Steps towards a global standard for Ordovician stratigraphy: Newsletters on Stratigraphy, v. 36, no. 1, p. 1-33.
- Zhang, E. and Davis, A., 1993, Coalification patterns of the Pennsylvania coal measures in the Appalachian foreland basin, western and south-central Pennsylvania: Geological Society of America Bulletin, v. 105, p. 162-174.